On the Bragg, Leibfried, and Modified Leibfried Numbers

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Abstract

The Bragg, Leibfried, and modified Leibfried numbers are defined in the context of a theory of dislocation-mediated melting, and their values are determined from the properties of the dislocation ensemble at the melting temperature. The approximate numerical coincidence of the Bragg and modified Leibfried numbers is explained. The parameter K in the definition of the modified Leibfried number is shown to be the natural logarithm of the effective coordination number. Our analysis reveals that the Bragg number can be considered an elemental constant, in contrast to the Leibfried and modified Leibfried numbers.

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In Leibfried's study of melting [1] he observed that for a number of metals (specifically Al, Ag, Au, Cu, Pd and Pb)

$$L \equiv RT_m/GV \simeq 0.042,\tag{1}$$

where R is the gas constant, T_m is the melting temperature, G is the ambient shear modulus, and V is the molar volume. The factor RT_m is an approximation to the heat of fusion, L_m , which follows from Richard's rule [2]

$$L_m/T_m = \triangle S_m \simeq 2.0 \text{ e.u.} \approx R$$
 (2)

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(1 e.u. = 1 cal/mol $^{\circ}$ K), since the numerical value of R is 1.987 e.u. Bragg [3], on the other hand, noted that

$$B \equiv L_m/GV \simeq 0.034 \tag{3}$$

for a few metals (specifically Al, Ag, Au, Co, Cu, Fe, Ni and Pb).

Although L, the Leibfried number, and B, the Bragg number, seem to be intrinsically related, through Richard's rule, there is a relatively large discrepancy between their values. The importance of both numbers in the calculation of the size factors caused Gschneidner to reanalyze them in his review [2]. First, he noticed that Richard's rule may not be a valid approximation. In fact, Stull and Sinke [4] had earlier used two different values for estimating heats of fusion, 2.3 e.u. for elements which crystallize as face-centered cubic (fcc) or hexagonal close-packed (hcp) structures, and 1.9 e.u. for elements which have body-centered cubic (bcc) structure. Second, Gschneidner introduced the modified Leibfried number, L', which differs from the Leibfried number L in that the term RT_m is replaced by the term KT_m . The value of K depends on the crystal structure of the element just below its melting point: 2.29 e.u. for fcc or hcp metals, 1.76 e.u. for bcc metals, etc. Finally, he concluded that the modified Leibfried and Bragg numbers do agree within uncertainties.

In this Technical Note we offer an explanation for the numerical values of both L' and B in a theory of dislocation-mediated melting. We obtain the numerical values of B, L and L' from the properties of the dislocation ensemble at the melting point. We also explain the approximate numerical coincidence of the values of L' and B.

In our previous study of melting as a dislocation-mediated phase transition on a lattice [5, 6], we obtained two relations:

$$k_B T_m = \frac{\lambda \kappa G v_{WS}}{8\pi \ln z'} \ln \left(\frac{\alpha^2}{4b^2 \rho(T_m)} \right), \tag{4}$$

$$L_m = \frac{1}{\lambda} b^2 \rho(T_m) R T_m \ln z', \tag{5}$$

where $\rho(T_m)$ is the critical dislocation density at melt, v_{WS} is the Wigner-Seitz volume, $1/\kappa = (1 - \nu/2) \pm \nu/2 \approx 5/6$, ν being the Poisson ratio, b is the shortest perfect-dislocation Burgers vector, $\lambda \equiv b^3/v_{WS} \approx 4/3$, and $\alpha = 2.9$ accounts for nonlinear effects in a dislocation core. Also, z', the effective coordination number for a dislocation as a random walk on the lattice, satisfies $z' \leq z$, where z is the coordination number of the lattice. These relations hold to $\sim 20\%$ accuracy for those elements of the Periodic Table (more than half) for which sufficient data exist.

It then follows that the Bragg number is

$$B = \frac{\kappa}{8\pi} b^2 \rho(T_m) \ln\left(\frac{\alpha^2}{4b^2 \rho(T_m)}\right). \tag{6}$$

We have found [6] that the critical dislocation density at melt is an elemental constant with an approximate numerical value of $2/3b^2$ for three-quarters of the Periodic Table. It

corresponds to the situation where, on average, half of the atoms are within a dislocation core at melt. Hence, the Bragg number must be an elemental constant, and its approximate numerical value is, in view of Eq. (6) with the numerical values of the parameters quoted above,

$$B \approx \frac{0.92}{8\pi} \approx 0.037,\tag{7}$$

in agreement with Bragg's original estimate. We discuss this point in more detail below. Similarly, the Leibfried number is

$$L = \frac{\lambda \kappa}{8\pi \ln z'} \ln \left(\frac{\alpha^2}{4b^2 \rho(T_m)} \right). \tag{8}$$

It depends, through $\ln z'$, on the crystal structure of the solid phase of the element from which melting occurs, in agreement with Gschneidner's observation. It is, however, possible to define modified Leibfried numbers that approximately coincide numerically with the Bragg number [2]:

$$L' \equiv \frac{K}{R}L,\tag{9}$$

where K may be defined in either of two ways:

$$K = \frac{2b^2 \rho(T_m) \ln z'}{\lambda} \text{ e.u.}$$
 (10)

or

$$K = \ln z' \text{ e.u.} \tag{11}$$

In the first case,

$$L' = \frac{\kappa}{4\pi} b^2 \rho(T_m) \ln \left(\frac{\alpha^2}{4b^2 \rho(T_m)} \right) \frac{\text{e.u.}}{R}$$
 (12)

will approximately coincide numerically with B given in Eq. (6), since the numerical value of R in units of e.u. is very close to 2. In the second case,

$$L' = \frac{\lambda \kappa}{8\pi} \ln \left(\frac{\alpha^2}{4b^2 \rho(T_m)} \right) \frac{\text{e.u.}}{R}$$
 (13)

will again approximately coincide numerically with B given in (6), since $R \approx 2$ e.u., $b^2 \rho(T_m) \approx 2/3$ and $\lambda \approx 4/3$.

In the first case, the numerical values of K in e.u., according to Eq. (10), are 2.26 for fcc and hcp metals (for which $\lambda = \sqrt{2}$ and z = 12) and 1.99 for bcc metals (for which $\lambda \approx 1.3$ and z = 8), where we have taken $b^2 \rho(T_m) = 2/3$ and z' = z - 1 [5, 6]. These values of K are consistent with those presented by Gschneidner, 2.29 and 1.76, respectively. In the second case, the corresponding values for z' = z - 1 are 2.40 for fcc and hcp metals and 1.95 for bcc metals, and for z' = z - 2 these values are 2.30 for fcc and hcp metals and 1.79 for bcc metals. It is therefore seen that in the second case the choice z' = z - 2 leads to better agreement between the values of K calculated from Eq. (11) and those given

by Gschneidner. This is not sufficient, however, to conclude that the choice z'=z-2 is better than the choice z'=z-1 used in [5, 6], since Gschneidner [2] did not specify the criteria for his choice of the values of K. Equation (5) with z'=z-1, for example, explains the Stull-Sinke rule, since it gives $L_m/T_m=2.25$ e.u. for fcc and hcp metals, and 1.98 e.u. for bcc metals, in good agreement with the values 2.3 e.u. and 1.9 e.u. used by Stull and Sinke. In any case, the uncertainty in the value of $\ln z'$ associated with the choice between $\ln(z-1)$ and $\ln(z-2)$ does not exceed 8%, which is well within the $\sim 20\%$ uncertainty of Eqs. (4),(5).

In ref. [5], for three-quarters of the Periodic Table, we established that

$$b^2 \rho(T_m) = 0.64 \pm 0.14. \tag{14}$$

It then follows from Eqs. (3)-(5) with z'=z-1 and the numerical values of the parameters quoted above, that

$$B = 0.0369 \pm 0.0093,\tag{15}$$

where most of the error comes from uncertainty in the value of κ . Hence, uncertainty in the numerical value of B is about 25%, which is sufficiently small that B can be considered an elemental constant.

As follows from Eqs. (1), (4) with z' = z - 1, and Eq. (14),

$$L = 0.0308 \pm 0.0113,\tag{16}$$

where we have used z = 8 and 12 to fix the error bar. Also, from using this value of L, the modified Leibfried number defined by Eqs. (9) and (11) with z' = z - 1 is

$$L' = 0.0337 \pm 0.0119,\tag{17}$$

where, again, the error reflects the two values of z. These values of L and L' are in agreement with the values obtained in ref. [2] for almost all the elements of the Periodic Table: $L = 0.0305 \pm 0.0135$, $L' = 0.0334 \pm 0.0145$. Although the values of B, L, and L' do agree within errors, uncertainties associated with both L and L' are about 35% which is so large that they cannot be considered elemental constants.

To conclude, we have defined and evaluated the Bragg, Leibfried and modified Leibfried numbers in the theory of dislocation-mediated melting. We have explained the approximate numerical coincidence of the Bragg and modified Leibfried numbers. We have shown that the Bragg number can be considered an elemental constant, in contrast to the Leibfried and modified Leibfried numbers. In our analysis, the quantity $\ln z'$ is identified with Gschneidner's constant K. The factor $\ln z'$ can only arise naturally in a theory of line-like defects.

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